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Packed bed chemical looping platform: design and operation of $30kW_{th}$ pilot unit

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Abstract

Chemical looping combustion is a novel flameless combustion, where the conventional combustion is divided into reducer and oxidizer with assistance of the oxygen carrier. Due to its instinctive CO_2 separation, high efficient and environmental-friendly property, chemical looping combustion attains more concerns. Large-scale experimental unit is a vital to chemical looping combustion, especially the commercial development. The reactor configuration of the worldwide pilot units are fluidized bed or moving bed, and the pilot unit with packed bed has not been reported. In this study, the pilot scale chemical looping packed bed unit with a nominal thermal capacity of $30kW_{th}$ is designed on the basis of previous laboratory scale investigation. The pilot unit includes four parts, which is gas system, reaction system, tail gas treatment and gas analysis system, and auxiliary electrical system. The pilot packed bed reactor is made from 310s stainless steel tube with a 0.089 m o.d., a 0.079 m i.d., and 2.0 m height. A K-type thermocouple with 13 measurement points is located at the center of the packed bed reactor to obtain the axial temperature profile. The packed bed chemical looping platform is constructed to demonstrate the feasibility of generating high purity hydrogen from syngas derived from biomass wastes with on-site carbon capture. Two testing runs were presented using 5 mm × 4-6 mm cylindrical oxygen carriers comprising of 50 wt % iron oxide (Fe_2O_3). The pure CO and the mixture of CO and H_2 with a flow of 15 SLPM are the fuels of the two tests. The first test resulted in a full CO conversion with a 25.0% conversion of the oxygen carriers during reduction, the production of 3.82 mol hydrogen with an average purity of 98.0%, and the maximum temperature rise is 219 K during air combustion. The second test leaded to a full fuel conversion with a 35.7% conversion of the oxygen carriers during reduction, the production of 4.67 mol hydrogen with an average purity of 98.0%, and the maximum temperature rise is 290 K during air combustion. The two testing runs, the first operation of packed bed chemical looping pilot unit, supported syngas-based chemical looping application for hydrogen and power co-generation with in suit carbon capture and also demonstrated the design of the $30kW_{th}$ pilot chemical looping platform with packed bed reactor.

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1. Introduction

Biomass is one kind of renewable energy which is regarded as a possible substitute for fossil fuel[1,2]. Biomass waste has the property of energy and pollution simultaneously. The energy utilization of biomass waste is vital meaning. In China, the annual production of biomass waste is nearly 5 billion tons[3,4]. Most of the biomass waste is difficult to biodegrade. Thermo-chemical technology is the main route to deal with these hard-biodegraded biomass waste. Due to low exergy efficiency and serious secondary pollution, the traditional combustion of biomass waste is limited. Thus, the biomass waste pyrolysis-chemical looping hydrogen generation process (p-CLHG) is proposed, which is low-carbon, low-NO_x and low dioxin[5,6].

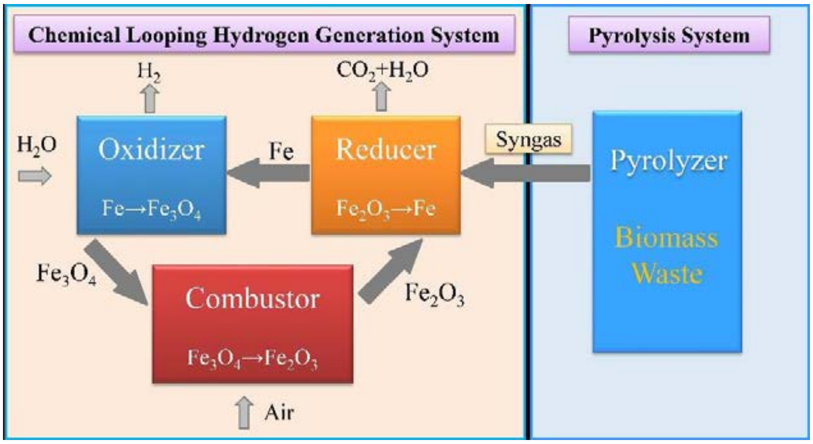

Fig. 1. The schematic diagram of biomass waste pyrolysis-chemical looping hydrogen generation process.

Fig. 1 shows the schematic diagram of the biomass waste p-CLHG process. In the pyrolysis reactor, biomass waste is pyrolyzed under anaerobic conditions to obtain the syngas. Syngas is used as the CLHG fuel, which carries out the capture of CO_2 during hydrogen generation. The p–CLHG process is attractive because it restrains the formation of dioxin, generates high purity hydrogen, and realizes carbon management.

The syngas CLHG includes fuel reduction, steam oxidization, and air combustion. And the oxygen carrier in CLHG is iron-based oxygen carrier. The theoretical reactions in the three steps are as follows.

Fuel reduction:

$$Fe_2O_3 + syngas \rightarrow Fe + CO_2 + H_2O \tag{1}$$

Steam oxidization:

$$Fe + H_2O \rightarrow Fe_3O_4 + H_2 \tag{2}$$

Air combustion:

$$Fe_3O_4 + Air \rightarrow Fe_2O_3 + N_2 \tag{3}$$

From these reactions, the CLHG is one kind of derived processes from chemical looping combustion (CLC)[7]. The test facility is vital to the development of CLC. The worldwide operating facilities are shown in Table 1[8]. It can be seen that the test facilities are main fluidized bed reactor[9-14], and the packed bed reactor[15-18], especially large-scale packed bed, is rare.

Table 1. The main information of worldwide operating facilities for CLC.

Location	Thermal input	Confign(air-fuel)	Fuel tested	Carriers tested
Chalmers U	300W	CFB-BFB	Natural gas, syngas	NiO, Mn_3O_4, Fe_2O_3, ilmenite
CSIC	500W	BFB-BFB	Natural gas	CuO, NiO
Eindhoven TU	100W	PB-PB	CH_4, Syngas	CuO, ilmenite
KAIST	1kW	BFB-BFB	CH_4	NiO+Fe_2O_3
CSIC	1.5kW	BFB-BFB	Coal, CH_4	NiO, CuO, Fe_2O_3
Chalmers U	10kW	CFB-BFB	Natural gas	NiO, Fe_2O_3
Chalmers U	10kW	CFB-BFB	Coal, petcoke	Ilmenite
Nanjing U	10kW	CFB-spouted bed	Coal, biomass	NiO, Fe_2O_3
Tsinghua U	10/50kW		Coal and gas	MeO_x, Calcium
IFP	10kW	BFB-BFB-BFB	CH_4	NiO
Univ. Stuttgart	10kW	CFB-BFB	Syngas	Ilmenite
Xi'an Jiaotong U	10kW	Press CFB-BFB	Coke oven gas	Fe_2O_3/CuO
OSU	25kW	EFR-moving bed	Coal	Fe_2O_3
Hamburg U	25kW	CFB-BFB/BFB	Coal	Ilmenite
Tsinghua U	30kW	PB-PB-PB	Syngas	Fe_2O_3 (this paper)
US DOE	50kW	CFB-CFB	Natural gas	Fe_2O_3, Cu-Fe oxide
KIER	50kW	CFB-BFB; BFB-CFB	Natural gas, syngas	NiO, CoO
Alstom	65kW	TR-TR	Coal, wood char	Limestone
Chalmers U	100kW	CFB-BFB-BFB	Coal	Ilimenite
Univ. Utah	100kW	Under construction	Coal	CuO
Vienna TU	140kW	CFB-CFB	Natural gas, CO, H_2	Ilimenite, NiO
OSU/NCCC	250kW	Under construction	Syngas	Fe_2O_3
Darmstadt U	1MW	CFB-CFB	Coal	Ilimenite
Alstom	3MW	TR-TR	Coal, wood char	Limestone

Where BFB-Bubbling Fluidized Bed, CFB-Circulating Fluidized Bed, PB-Packed Bed, TR-Transport Reactor

In this study, a 30 kW_{th} packed bed chemical looping platform is designed and operated. The design procedure of the 30kWth chemical looping reactor is introduced firstly. Then the chemical looping pilot unit is constructed according to the design results. Finally, two tests with different fuel and different loading scheme are running to explore the feasibility of CLHG in packed bed platform and also demonstrate the design of 30 kW_{th} pilot unit.

2. Design and construction of chemical looping pilot unit

2.1. Chemical looping reactor design

In packed bed chemical looping unit, the oxygen carrier particles are packed into the reactor and they are alternately exposed to the reducing and oxidizing conditions via periodic switching of the gas feed streams[19]. Several reactors operating in parallel to assure a continuous gas stream production. In this mode, each reactor experiences the same operating steps, so the design of these parallel reactors are same.

The loading quality of the oxygen carrier particles in the packed bed reactor is confirmed according to the thermal power. To ensure the plug flow operation, the reactor length to diameter ratio should be 10[20]. Combined with the loading quality, bulk density of the oxygen carrier particles, and the specified length to diameter ratio, the diameter of packed bed reactor is 80mm.

The gas flow is determined to meet the two requirements: (1) the pressure drop is less than 15% of the bed pressure; (2) enough resistance time. Based on the gas flow, the sizes of pipeline, valve, and other auxiliary devices are calculated.

2.2. Construction of chemical looping pilot unit

The packed bed chemical looping pilot unit includes four parts, which is gas system, reaction system, tail gas treatment and gas analysis system, and auxiliary electrical system.

The gas system supply the quantitative gas to the reaction system. It contains globe valve, pressure gage, reducing valve, mass flow controller, solenoid valve, check valve and pipeline. The main involved gas is CO, H_2, N_2 and air.

The reaction system is the core of the pilot unit, it is the place where the chemical looping reaction happens. It includes 310s stainless steel tube and electric heating furnace. The electric heating furnace contains four parts, and their power is 4, 4, 6 and 4kW, respectively.

The tail gas treatment and gas analysis system is used to obtain the concentration of the tail gas. The tail gas is firstly cooled to separate the water. After that, the gas is dried by desiccant. The dry gas is metered and then sent to the gas analyzer.

The auxiliary electrical system provides the essential dynamic electricity and signal electricity to assure the running of pilot unit.

The 30 kW_{th} packed bed chemical looping pilot unit is presented in Fig.2. It located at Tsinghua University in Beijing. The iron-based oxygen carriers loaded in the pilot unit are utilized to process syngas derived from biomass waste and generate high purity hydrogen.

Fig. 2. Photograph of 30 kW_{th} CLHG unit at Tsinghua University.

3. Experimental section

3.1. Oxygen carrier

The iron-based oxygen carriers Fe_2O_3/Al_2O_3 used in this study is prepared through a mechanical mixing method. Fe_2O_3 and Al_2O_3 were firstly mixed at a specified weight ratio, the mass ratio of Fe_2O_3 to Al_2O_3 was set to 50:50. Then processed by wet ball milling at 150 rpm for 3 hours. Then the produced paste was dried at 105°C for 12 hours before calcination. The dry powder was tableted by a T-AII single-punch tablet press at 18Hz. The tableting particle is 5 mm × 4-6 mm cylinder. Iron-based oxygen carriers were calcinated at 1173 K for 10 hours prior to loading in the packed bed reactor. Fig.1 shows the preparation process of iron-based oxygen carrier.

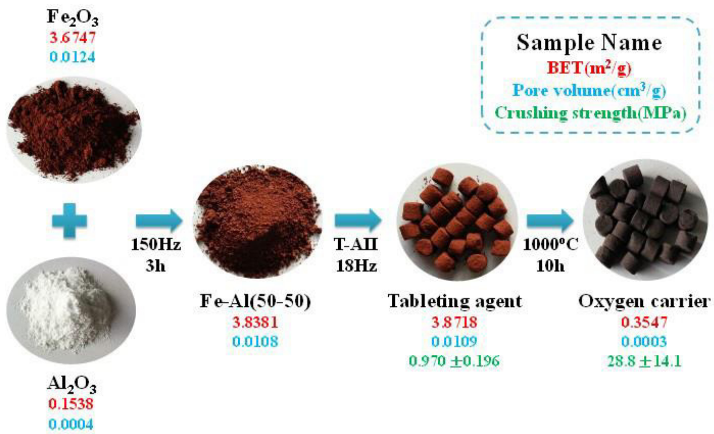

Fig. 3. Preparation process of iron-based oxygen carrier.

3.2. Chemical looping pilot operation

A pilot-scale packed bed reactor is used to test the chemical looping hydrogen generation reactor operation. The packed bed reactor was made from a 310s stainless tube (a 0.089 m o.d., a 0.079 m i.d., and 2.0 m height) as shown in Fig. 4. The packed bed reactor includes three layers, which is supporting layer, packing layer, and optional thermal storage layer. The entire assembly was placed in a tubular furnace and the temperature of the bed was controlled by a K-type thermocouple with 13 measurement points which is located at the center of the packed bed reactor. Reactant gases are introduced from the gas inlet located at the top of the packed bed and react with the oxygen carrier. The composition of dry gas is continuously monitored by an ONUEE multichannel gas analyzer.

To explore the feasibility of CLHG in packed bed platform and also demonstrate the design of 30 kW_{th} pilot unit, two tests with different fuel and different loading scheme are running at ambient pressure and 800 °C. Before the experiments, 3 kg alumina ball with 10 mm diameter and 4 kg iron-based oxygen carrier particle are loaded in sequence from the bottom of the bed, which act as the supporting layer and packing layer, respectively. The length of the supporting layer and packing layer is 495 and 475 mm. For test 2, 3kg alumina ball with 10 mm diameter is loaded on the top of packing layer as the thermal storage layer. Its length is 495 mm. While heating up the reactor, the N_2 is introduced into the packed bed at a flow rate of 15 L/min as purging gas. The reduction of the iron oxide particles was performed using pure CO and syngas with a flow rate of 15 L/min for test 1 and test 2. The syngas for test 2 contains CO and H_2, and the mole ratio of CO and H_2 is 1:1. The reduction stops when the fuel slip happens. Then 30 g/min liquid water is pumped into the reactor to oxidize the reduced oxygen carrier, and N_2 with a flow of 5 L/min is also introduced as carrying gas. The steam oxidization is conducted until there is no hydrogen production. The reduced oxygen carrier was finally oxidized by air at a flow rate of 15 L/min. When the tail gas become air, the air combustion is completed. The N_2 at a flow rate of 15 L/min was used for purification after the reduction and combustion. All the flow rates of gases were controlled by mass flow controller.

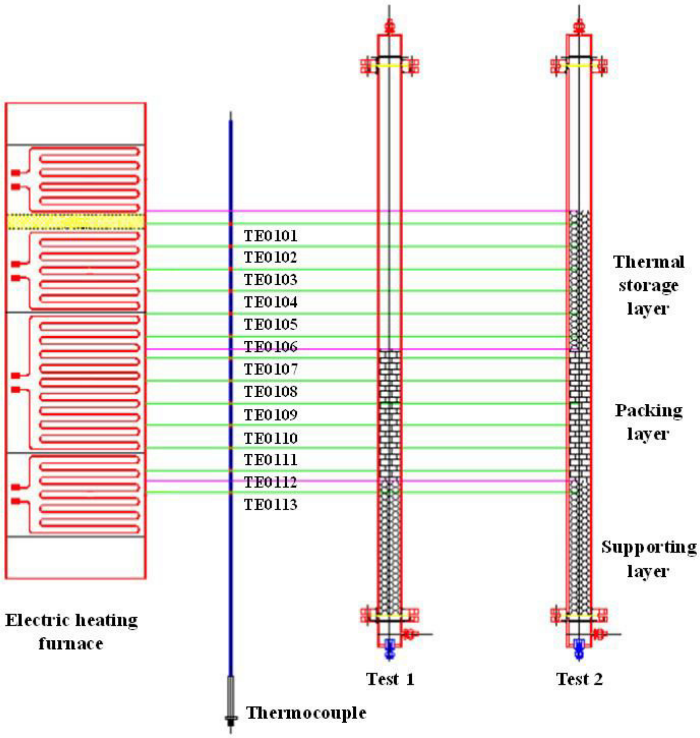

Fig. 4. Schematic diagram of CLHG process (a) without thermal storage layer and (b) with thermal storage layer configuration.

4. Results and discussions

4.1. Reduction behavior

The Fe_2O_3/Al_2O_3 is loaded in the pilot unit for CLHG. The fuel used for reducing Fe_2O_3/Al_2O_3 is pure CO and the syngas. Fig.5 shows the concentration profiles of tail gases during reduction process. The pure CO and syngas can be fully converted during reduction step in the 30 kW_{th} packed bed chemical looping pilot unit. For CO and syngas, the breakthrough time is 14 min and 20 min, respectively. It indicates that the reactivity of syngas is better that pure CO. From Fig.5 (b), the breakthrough time of CO and H_2 is 20min and 28min, so the slip of CO occurs before H_2.

The solid conversion of Fe_2O_3/Al_2O_3 in reduction step can be obtained from the consumption of fuel. Based on the mass balance, the solid conversion of Fe_2O_3/Al_2O_3 for CO and syngas at the breakthrough point is 25.0% and 35.7%. And the solid conversion of the whole reduction for CO and syngas is 29.5% and 46.7%.

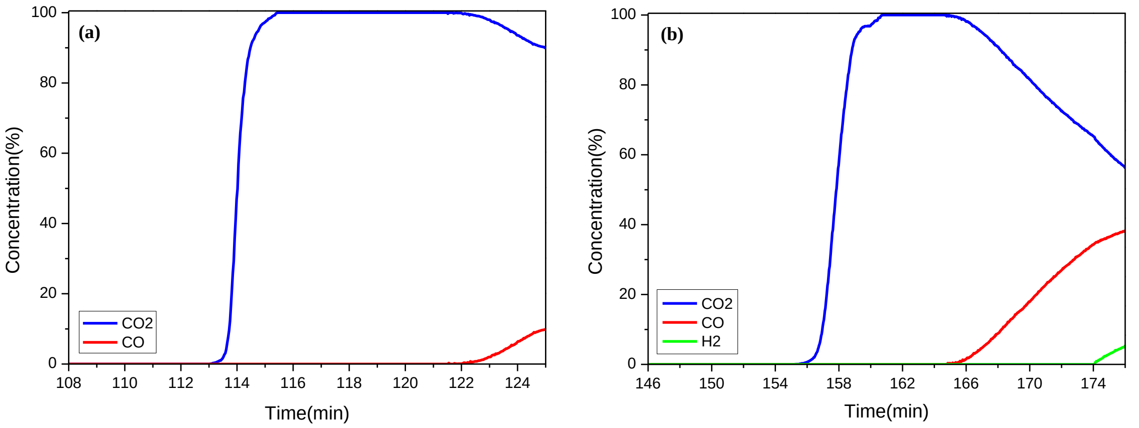

Fig. 5. Concentration profile of reduction process with (a) CO and (b) syngas ($CO:H_2$=1:1) as fuel.

4.2. Production of high purity hydrogen

The reduced Fe_2O_3/Al_2O_3 is oxidized by steam to produce hydrogen. Fig.6 presents the concentration profile of produced hydrogen during steam oxidization process. Steam oxidization process can generate high purity hydrogen.

For pure CO, the maximum hydrogen concentration is 99.1%, and 3.82 mol hydrogen with an average purity of 98.0% is generated. There are two hydrogen peaks in Fig.6 (a). It is caused by that the thermal storage layer is not loaded for CO as fuel. The liquid water will direct contact with the packing layer, the temperature of packed layer decrease which will stop the reaction between water and reduced oxygen carrier. To complete steam oxidization, the liquid water is re-injected to produce hydrogen when the packing layer is re-heated to 800 ºC. So the second hydrogen peak appears.

For syngas, the maximum hydrogen concentration is 99.2%, and 4.67 mol hydrogen with an average purity of 98.0% is generated. Notably, the concentration of carrying gas N_2 is not presented in Fig.6.

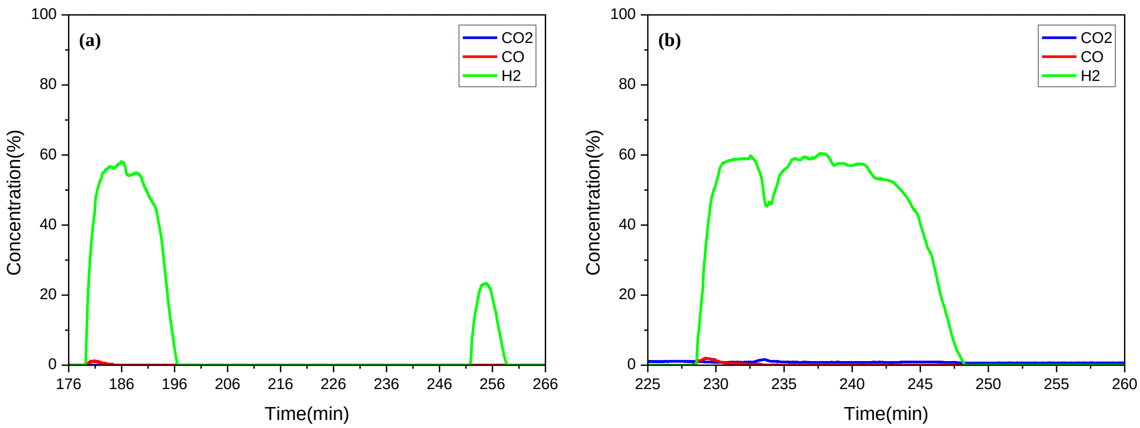

Fig. 6. Concentration profile of hydrogen generation process with (a) CO and (b) syngas (CO: H_2=1:1) as fuel.

4.3. Combustion behavior

To finally oxidize the reduced Fe_2O_3/Al_2O_3, the air is introduced to the unit. Fig.7 shows the concentration profile of air combustion process. The combustion time is about 30min. The O_2 breakthrough curves of CO and syngas are similar. Some CO and CO_2 appear in Fig.7, which indicates that some carbon deposition was formed during reduction process.

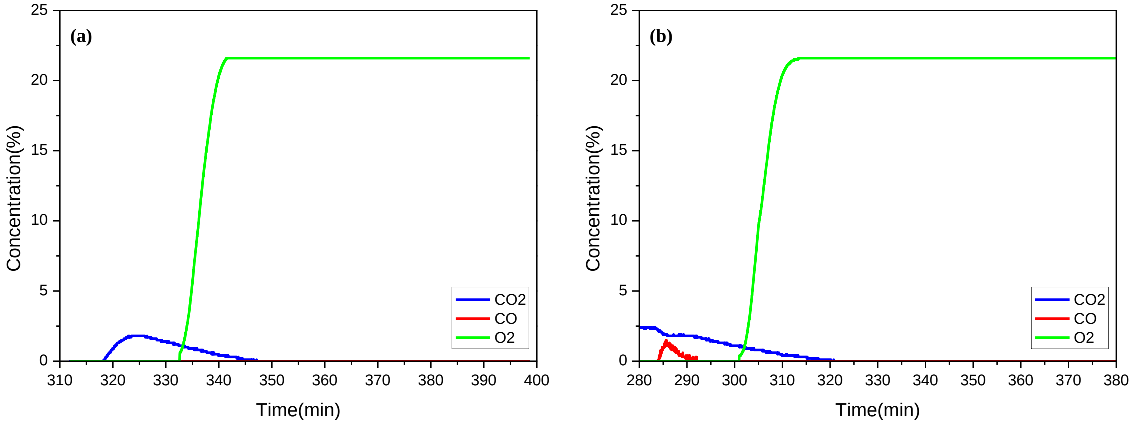

Fig. 7. Concentration profile of combustion process with (a) CO and (b) syngas (CO: H_2=1:1) as fuel.

The temperature profiles of combustion process are shown in Fig.8. Obvious temperature rise and temperature frontier movement appear during air combustion process. The maximum temperature rise for CO and syngas as fuel is 219 K and 290 K. The temperature frontier movement indicates that reaction frontier exists in the packing layer.

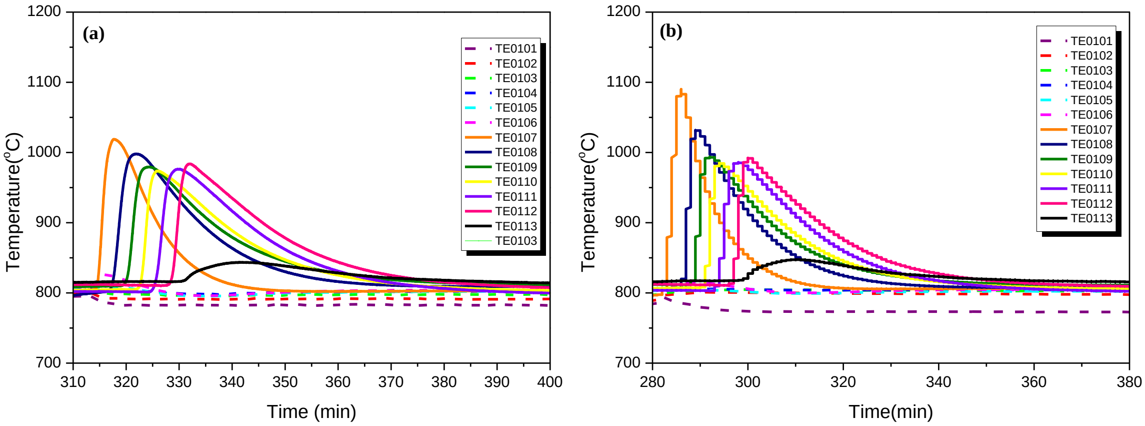

Fig. 8. Temperature profile of combustion process with (a) CO and (b) syngas (CO: H_2=1:1) as fuel.

4.4. Effect of thermal storage layer

In the steam oxidization step of CLHG, the feed is liquid water. When the liquid water direct contact with the packing layer, the temperature of packed layer decrease which will stop the reaction between water and reduced oxygen carrier, as presented in section 4.2. To avoid this phenomenon, the thermal storage layer is added at the top of the packing layer. The effect of thermal storage layer is shown in Fig.9.

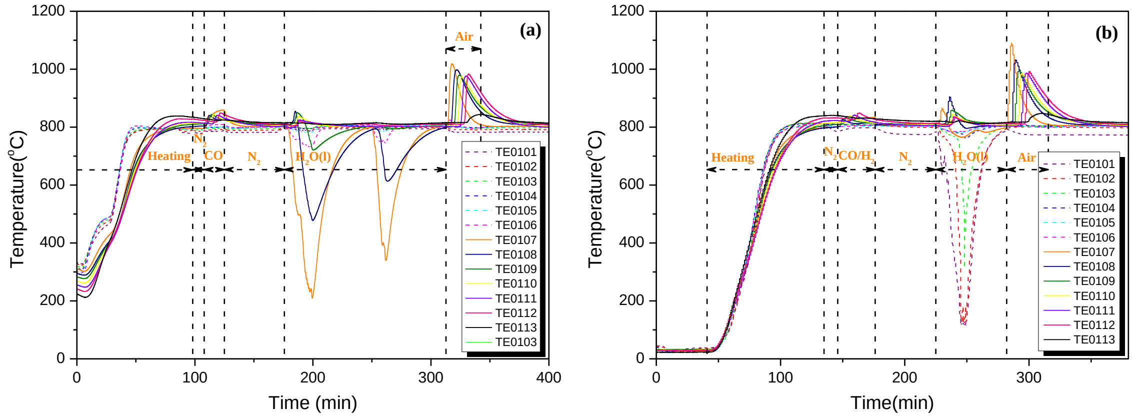

Fig. 9. Temperature profile of CLHG process (a) without thermal storage layer and (b) with thermal storage layer configuration.

Fig.9 (a) is the axial temperature profile of the packed bed reactor during the whole CLHG process for text 1, which the reactor without thermal storage layer. From Fig.5 (a), the value of TE0107, TE0108, and TE0109 decrease when the liquid water inject. As shown in Fig.4, the value of TE0107, TE0108, and TE0109 correspond the temperature of packing layer, i.e., the reaction zone. The temperature decrease leads to the termination of the hydrogen generation, shown in Fig.6 (a). After loading the thermal storage layer, the temperature of packing layer is relatively stable when the liquid water pumped, as shown in Fig.9 (b).

The effect of thermal storage layer on the temperature of packing layer can also be found from the heat load of electronic heating furnace corresponding to packing layer. From Fig.10, the heat load for thermal storage layer is more stable than that without thermal storage layer, which indicates that the temperature of packing layer is stable for thermal storage layer configuration.

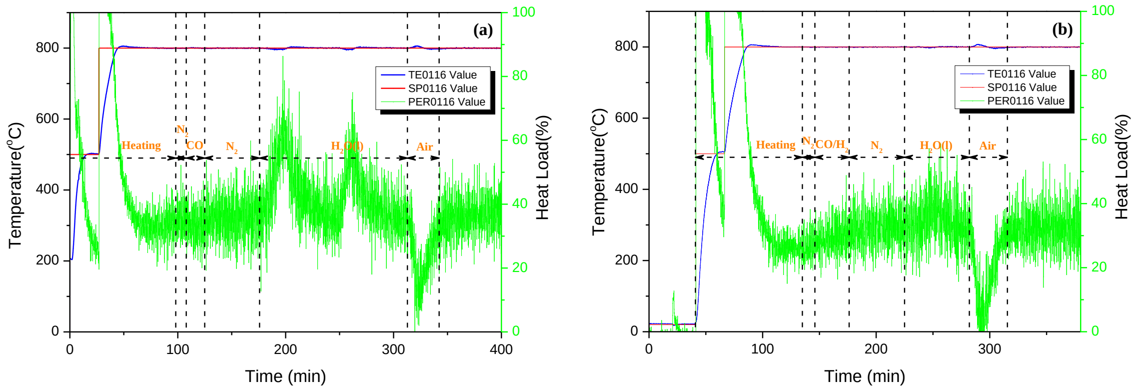

Fig. 10. Behavior of electric heating furnace in CLHG process (a) without thermal storage layer and (b) with thermal storage layer configuration.

5. Conclusions

30 kW_{th} packed bed chemical looping platform is designed and constructed to demonstrate the feasibility of generating high purity hydrogen from syngas derived from biomass wastes with on-site carbon capture. Two testing runs were presented using pure CO and the mixture of CO and H_2 as fuel. The first test resulted in a full CO conversion with a 25.0% conversion of the oxygen carriers during reduction, the production of 3.82 mol hydrogen with an average purity of 98.0%, and the maximum temperature rise is 219 K during air combustion. The second test leaded to a full

fuel conversion with a 35.7% conversion of the oxygen carriers during reduction, the production of 4.67 mol hydrogen with an average purity of 98.0%, and the maximum temperature rise is 290 K during air combustion. The two testing runs validate the feasibility of p-CLHG and also demonstrated the design of the $30kW_{th}$ packed bed chemical looping platform.

Acknowledgements

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